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(54) **FOAMED GASKETS MADE FROM HOMOGENEOUS OLEFIN POLYMERS**

**GESCHÄUMTE DICHTUNGEN AUS HOMOGENEN OLEFINPOLYMEREN**

**JOINTS D'ETANCHEITE MOUSSES FABRIQUES A PARTIR DE POLYMERES OLEFINIQUES  
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## Description

- [0001] This invention relates to foamed gaskets made from homogeneously branched olefin polymers, especially novel elastic substantially linear olefin polymers. The gaskets are capable of compression sealing various containers, without contaminating the contents. Liquid containers particularly benefit from the use of the novel gasketing materials disclosed herein.
- [0002] Gaskets have been made from a variety of structural materials, including polymers such as ethylene/vinyl acetate (EVA) and polyvinyl chloride (PVC). For example, USP 4,984,703 (Burzynski) discloses plastic closures which have a sealing liner comprising a blend of ethylene/vinyl acetate and a thermoplastic elastomeric composition.
- [0003] Depending on the use environment, gaskets can have varying degrees of properties. For example, in corrosive service conditions, the gasket must be impervious to the material in question, but still resilient enough to form a seal. Gaskets used in the food and beverage area have similar requirements, but cannot contaminate the foodstuff. Furthermore, depending upon the type of food and/or liquid contents, the filling temperature might be lower or higher than room temperature, thus placing greater demands on the gasket.
- [0004] Various attempts to solve these challenges usually involve the use of oil additives or elastomer additives.
- [0005] For example, USP 5,137,164 (Bayer) discloses a method of lining a plastic closure to with a thermoplastic. The thermoplastic is a non-cross linked curable, vinyl chloride copolymer composition which has been plasticized with an epoxidized oil, an organic diglycidyl ether and a curing agent for the ether.
- [0006] USP 4,807,772 (Schloss) and USP 4,846,362 (Schloss) disclose polypropylene and polyethylene closures, respectively, each having removable liners made from a blend of polyethylene and a thermoplastic, elastomeric copolymer (such as a block copolymer of styrene and butadiene). The blends are said to generally include 20-50 weight percent oil.
- [0007] USP 4,872,573 (Johnson et al.) discloses barrier layers for closures selected from the group consisting of ethylene/vinyl alcohol copolymers and polyvinylidene chloride, especially for retarding oxygen containing gases' migration.
- [0008] USP 5,000,992 (Kelch) discloses a plastic container closure made from a coextruded multilayer foamed film. The film has at least one solid layer of a polyethylene blend and at least one foamed layer of a second polyethylene blend. The polyethylene blends can be blends of linear low density polyethylene (LLDPE) and low density polyethylene (LDPE). This type of a liner is co-extruded using a blown film or cast film process, unlike the process disclosed and claimed herein. The polymer blend (foamed & unfoamed layers) is used to laminate to other materials such as polyester or metallic films.
- [0009] USP 3,786,954 (Shull) discloses laminated gaskets comprising a combination of a thick foamed polyethylene sheet material and a thin air and moisture impervious SARAN™ (trademark of and made by The Dow Chemical Company) layer adhered to the polyethylene by a low density polyethylene (LDPE) bond.
- [0010] USP 5,104,710 (Knight) discloses improvement of gasket adhesion through use of propylene adhesion promoters. Knight also discloses a linear low density polyethylene (LLDPE) as a comparison example and shows that it has insufficient bond temperature of 200°C.
- [0011] USP 4,529,740 (Trainor) discloses foamable structures made from elastomers such as styrene-butadiene block copolymers, a small amount of a salt of a sulfonated styrene polymer, and a blowing agent.
- [0012] USP 4,744,478 (Hahn) discloses a molded closure comprising at least one substantially unfoamed polymer layer and an integrally molded foamed layer of the same polymer. The polymer can be olefins, styrenics, polyesters, polycarbonates, or other suitable engineering resins. A preferred polymer is a copolymer of propylene and EDPM rubber.
- [0013] Polyvinyl chloride (PVC) polymers have also been used extensively as food closure gaskets, but these are increasingly coming under environmental pressures. Other polymers have also been used for their softness qualities, such as ethylene/methacrylic acid or ethylene/acrylic acid copolymers, but these often times contribute negatively to taste and odor problems, since the polymeric gasket comes in contact with the food and certain polymeric constituents leach into the food.
- [0014] Higher density polyethylene (HDPE) also has been disclosed as useful for forming gaskets, since the higher density polyethylene has relatively good taste and odor properties, but has not been commercially successful to date, because the polymer is too "hard" and because by adding oil to reduce the hardness, the extractables increase, thus negating regulatory requirements for food contact. In addition, while heterogeneous linear low density polyethylene (LLDPE) has better softness properties than HDPE, this LLDPE does not adhere well to certain plastic closures (for example, polypropylene, which is often used as a closure material, as described in USP 4,807,772) resulting in a loose polyethylene gasket. Further, this heterogeneous LLDPE, depending on the polymer's density, can also adversely affect taste and odor.
- [0015] While there have been many different solutions to the problems of gasketing materials, most of these incorporated additives causing other problems. We have now discovered foamed substantially linear ethylene polymers

useful in making gasket materials, without additives and, in the case of foodstuff, without adversely contributing to the taste and/or odor of the product.

[0016] Foamed gaskets comprising at least one blowing agent, and at least one homogeneously branched linear or homogeneously branched substantially linear olefin polymer have now been discovered to have these often conflicting attributes.

[0017] Therefore, the invention provides a foamed gasket characterized as comprising at least one homogeneously branched ethylene polymer and at least one blowing agent, wherein the polymer has a density of from 0.85 to 0.93 g/cm<sup>3</sup>, and is characterized as having a molecular weight distribution  $M_w/M_n$  of from 1.5 to 2.5 and as having a CDBI (Composition Distribution Branch Index) greater than 50 percent, which CDBI is calculated from data obtained by temperature rising elution fractionation. The homogeneously branched olefin polymers have an unusual combination of properties, making them especially useful for gasket materials. Preferably, the homogeneously branched olefin polymer is an ethylene polymer and more preferably, an ethylene/alpha-olefin copolymer.

[0018] The homogeneously branched substantially linear ethylene polymers have the processability similar to highly branched low density polyethylene (LDPE), but the strength and toughness of linear low density polyethylene (LLDPE). However, the homogeneously branched substantially linear olefin polymers are distinctly different from traditional Ziegler polymerized heterogeneous polymers (for example, LLDPE) and are also different from traditional free radical/high pressure polymerized highly branched LDPE. Surprisingly, the novel substantially linear olefin polymers are also different from linear homogeneous olefin polymers having a uniform branching distribution.

[0019] The substantially linear ethylene polymers used in the present invention are characterized as having various properties, alone or in combination:

- a) a melt flow ratio,  $I_{10}/I_2 \geq 5.63$ ,
- b) a molecular weight distribution,  $M_w/M_n$ , defined by the equation:

$$M_w/M_n \leq (I_{10}/I_2) - 4.63,$$

and

- c) a critical shear stress at onset of gross melt fracture greater than  $4 \times 10^6$  dyne/cm<sup>2</sup>,

- d) a critical shear rate at onset of surface melt fracture at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear ethylene polymer having about the same  $I_2$ , density, and  $M_w/M_n$ , and/or

- e) a processing index (PI) less than or equal to about 70 percent of the PI of a comparative linear ethylene polymer at about the same  $I_2$ , density, and  $M_w/M_n$ .

[0020] The gaskets of the invention preferably comprise at least one substantially linear ethylene polymer having a polymer backbone which is substituted with from 0.01 to 3 long chain branches per 1,000 carbons which is further characterized as having the above features a), b) and c).

[0021] Gaskets comprising elastic substantially linear ethylene polymers are especially preferred. A complete olefinic system (such as a foamed gasket comprising the substantially linear ethylene polymer and a cap comprising a polyethylene or polypropylene polymer) can also be recycled together. Potential uses of the recycled polymers include melt spinning biconstituent fiber, as described in USP 5,133,917 (Jezic et al.).

[0022] The term "linear ethylene polymers" used herein means that the ethylene polymer does not have long chain branching. That is, the linear ethylene polymer has an absence of long chain branching, as for example, the traditional heterogeneous linear low density polyethylene polymers or linear high density polyethylene polymers made using Ziegler polymerization processes (for example, USP 4,076,698 (Anderson et al.), sometimes called heterogeneous polymers. The Ziegler polymerization process, by its catalytic nature, makes polymers which are heterogeneous, that is, the polymer has several different types of branching within the same polymer composition as a result of numerous metal atom catalytic sites. In addition, the heterogeneous polymers produced in the Ziegler process also have broad molecular weight distributions (MWD); as the MWD increases, the  $I_{10}/I_2$  ratio concurrently increases.

[0023] The term "linear ethylene polymers" does not refer to high pressure branched polyethylene, ethylene/vinyl acetate copolymers, or ethylene/vinyl alcohol copolymers which are known to those skilled in the art to have numerous long chain branches. The term "linear ethylene polymers" can refer to polymers made using uniform branching distribution polymerization processes, sometimes called homogeneous polymers. Such uniformly branched or homogeneous polymers include those made as described in USP 3,645,992 (Elston) and those made using so-called single site catalysts in a batch reactor having relatively high olefin concentrations (as described in U.S. Patent 5,026,798 (Canich) or in U.S. Patent 5,055,438 (Canich)) or those made using constrained geometry catalysts in a batch reactor also having relatively high olefin concentrations (as described in U.S. Patent 5,064,802 (Stevens et al.) or in EPA 0 416 815 A2 (Stevens et al.)). The uniformly branched/homogeneous polymers are those polymers in which the comonomer

is randomly distributed within a given interpolymer molecule and wherein substantially all of the interpolymer molecules have the same ethylene/comonomer ratio within that interpolymer, but these polymers too have an absence of long chain branching.

[0024] The term "substantially linear" polymers means that the polymer has long chain branching and that the polymer backbone is substituted with 0.01 long chain branches/1000 carbons to 3 long chain branches/1000 carbons, more preferably from 0.01 long chain branches/1000 carbons to 1 long chain branches/1000 carbons, and especially from 0.05 long chain branches/1000 carbons to 1 long chain branches/1000 carbons. Similar to the traditional linear homogeneous polymers, the substantially linear ethylene/ $\alpha$ -olefin copolymers used in this invention also have a homogeneous branching distribution and only a single melting point, as opposed to traditional Ziegler polymerized heterogeneous linear ethylene/ $\alpha$ -olefin copolymers which have two or more melting points (determined using differential scanning calorimetry (DSC)). The substantially linear ethylene polymers are described in USP 5,272,236 and USP 5,278,272.

[0025] Long chain branching for the substantially linear ethylene polymers is defined herein as a chain length of at least 6 carbons, above which the length cannot be distinguished using  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy. The long chain branch of the substantially linear ethylene polymers is, of course, at least one carbon longer than two carbons less than the total length of the comonomer copolymerized with ethylene. For example, in an ethylene/1-octene substantially linear polymer, the long chain branch will be at least seven carbons in length. However, the long chain branch can be as long as about the same length as the length of the polymer backbone. For substantially linear ethylene/ $\alpha$ -olefin copolymers, the long chain branch is also itself homogeneously branched, as is the backbone to which the branch is attached.

[0026] The SCBDI (Short Chain Branch Distribution Index) or CDBI (Composition Distribution Branch Index) is defined as the weight percent of the polymer molecules having a comonomer content within 50 percent of the median total molar comonomer content. The CDBI of a polymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation (abbreviated herein as "TREF") as described, for example, in Wild et al, *Journal of Polymer Science, Poly. Phys. Ed.*, Vol. 20, p. 441 (1982), or as described in U.S. Patent 4,798,081. The SCBDI or CDBI for the homogeneously branched linear or homogeneously branched substantially linear olefin polymers of the present invention is greater than 50 percent, preferably greater than 80 percent, and especially greater than 90 percent.

[0027] The density of the homogeneously branched linear or homogeneously branched substantially linear ethylene or ethylene/ $\alpha$ -olefin polymers in the present invention is measured in accordance with ASTM D-792 and is generally from 0.85 g/cm<sup>3</sup> to 0.93 g/cm<sup>3</sup>, preferably from 0.895 g/cm<sup>3</sup> to 0.92 g/cm<sup>3</sup>, and especially from 0.895 g/cm<sup>3</sup> to 0.915 g/cm<sup>3</sup>.

[0028] The density is obviously related to the amount of comonomer incorporated into the polymer; the higher the comonomer incorporated, the lower the density. The Food and Drug Administration (FDA) currently limits hexane extractables for polyethylene for food contact to not more than 5.5 percent. The method is described in FDA regulation 21 CFR Ch. 1(4-1-94 Edition) §177.1520, pages 252-253. Even though molecular weight distribution influences hexane extractables, larger amounts of comonomer, especially for heterogeneous polyethylene copolymers, causes higher levels of hexane extractables. For example, a heterogeneous ethylene/1-octene linear polyethylene having densities from 0.9017 to 0.91 g/cm<sup>3</sup> generally have hexane extractables greater than 5 percent. In contrast, for example, a homogeneous substantially linear ethylene/1-octene copolymer having a density at least as low as 0.8976 g/cm<sup>3</sup> and a melt index of 1g/10 minutes, has hexane extractables less than 5 percent, preferably less than 2 percent and especially less than 1 percent.

[0029] Melting point (and Vicat softening point) of the substantially linear ethylene polymers correlates primarily with the density of the polymer since the substantially linear ethylene polymers lack a high density (that is, non-short chain branched) fraction, with some effects attributable to the molecular weight of the polymer (indicated melt index). Melting point variation of the substantially linear ethylene polymers is contrasted with heterogeneous ethylene polymers having two or more melting points (due to their broad branching distribution), one of which is about 126°C and is attributable the high density linear polyethylene fraction. The lower the density of the substantially linear ethylene polymer, the lower the melting point. For example, Table 1 lists Vicat softening point (as measured using ASTM D-1525) versus density for various substantially linear ethylene/1-octene copolymers:

Table 1

Density (gm/cm <sup>3</sup> )	Vicat Softening Point (°C)
0.939	125
0.922	100
0.903	84

Table 1 (continued)

Density (gm/cm <sup>3</sup> )	Vicat Softening Point (°C)
0.886	63
0.884	58
0.872	44

Some gaskets must withstand temperatures higher than room temperature (about 25°C) for brief times, particularly where the application is a "hot fill" application. For example, products which must undergo pasteurization must have gaskets that have melting points greater than 100°C. Thus the substantially linear ethylene polymer can be selected specifically for the application in question by selecting the appropriate density for use in the gasket environment.

**[0030]** The molecular weight of the homogeneously branched linear or homogeneously branched substantially linear ethylene or ethylene/α-olefin polymers used in the present invention is conveniently indicated using a melt index measurement according to ASTM D-1238, Condition 190°C/2.16 kg (formally known as "Condition (E)" and also known as I<sub>2</sub>). Melt index is inversely proportional to the molecular weight of the polymer. Thus, the higher the molecular weight, the lower the melt index, although the relationship is not linear. The melt index for the ethylene or ethylene/α-olefin homogeneously branched linear or homogeneously branched substantially linear olefin polymers used herein is generally from 0.01 grams/10 minutes (g/10 min) to 1000 g/10 min, preferably from 1 g/10 min to 100 g/10 min, and especially from 3 g/10 min to 50 g/10 min. Molecular weight, as indicated by the melt index, will be dependent upon the shear rate necessary to process the polymer into the gasket.

**[0031]** Another measurement useful in characterizing the molecular weight of the homogeneously branched linear or homogeneously branched substantially linear olefin polymers is conveniently indicated using a melt index measurement according to ASTM D-1238, Condition 190°C/10 kg (formerly known as "Condition (N)" and also known as I<sub>10</sub>). The ratio of these two melt index terms is the melt flow ratio and is designated as I<sub>10</sub>/I<sub>2</sub>. For the substantially linear ethylene/α-olefin polymers of the invention, the I<sub>10</sub>/I<sub>2</sub> ratio indicates the degree of long chain branching, that is, the higher the I<sub>10</sub>/I<sub>2</sub> ratio, the more long chain branching in the polymer. Generally, the I<sub>10</sub>/I<sub>2</sub> ratio of the substantially linear ethylene/α-olefin polymers is at least 5.63, preferably at least 7, especially at least 8 or above. The upper limit of the I<sub>10</sub>/I<sub>2</sub> ratio can be 50, preferably 20, and especially 15.

**[0032]** For gaskets made from the preferred substantially linear ethylene polymers, the melt flow ratio (I<sub>10</sub>/I<sub>2</sub>) can be increased to compensate for the use of higher molecular weight polymers (that is, lower melt index polymers). Other elastic properties of the homogeneously branched substantially linear ethylene polymers are also important, especially when the gasket is a closure liner, where higher amounts of long chain branching yields lower viscoelastic recovery (more inelastic), such that the polymer, when plunged into a closure, will adhere to the closure, rather than "bounce" out of the closure during fabrication.

**[0033]** Other polymers can also be combined with effective amounts of the homogeneously branched linear or homogeneously branched substantially linear ethylene polymers to make the gaskets as well, depending upon the end use properties required. These other polymers are thermoplastic polymers (that is, melt processable) and include polymers such as highly branched low density polyethylene, heterogeneously branched linear low density polyethylene, ethylene/vinyl acetate copolymers, ethylene/α-olefin/diene ("EPDM") interpolymers, thermoplastic vulcanizates ("TPV's") (for example, EPDM blended with polypropylene cured by using sulfur or peroxide curing agents), thermoplastic rubbers, such as styrene/butadiene rubber (for example, KRATON® made by Shell Oil Company) and ethylene/acrylic acid copolymers (for example, PRIMACOR™ Adhesive Polymers made by The Dow Chemical Company). Oil may also be added, depending on the end use.

**[0034]** The gaskets made from the homogeneously branched linear or homogeneously branched substantially linear ethylene polymers must be hard enough to withstand compression, but still soft enough such that an adequate seal is formed. Thus, the hardness of the polymer enables varying gaskets to be made, depending on the use. Hardness is measured herein as "Shore A" hardness (as determined using ASTM D-2240). For the homogeneously branched linear or homogeneously branched substantially linear ethylene polymers which comprise the gaskets, the Shore A hardness ranges from 70 to 100, even without the use of petroleum oils commonly included to reduce the hardness of the polymer and resulting gasket. For the foamed gaskets made herein, the Shore A ranges from 40 to 95. Table 2 summarizes Shore A data versus polymer density for substantially linear ethylene/1-octene copolymers used to make gaskets:

Table 2

Polymer Density (g/cm <sup>3</sup> )	Shore A Hardness
0.87	73

Table 2 (continued)

Polymer Density (g/cm <sup>3</sup> )	Shore A Hardness
0.871	75
0.884	85
0.886	87
0.902	93
0.908	95
0.912	95
0.922	96
0.94	97

[0035] Additives such as antioxidants (for example, hindered phenolics (for example, Irganox® 1010 made by Ciba Geigy Corp.), phosphites (for example, Irgafos® 168 made by Ciba Geigy Corp.)), cling additives (for example, PIB), slip additives (for example, erucamide), antiblock additives, and pigments, can also be included in the homogeneously branched linear or homogeneously branched substantially linear polyethylene compositions, to the extent that they do not interfere with the enhanced properties discovered by Applicants.

#### Molecular Weight Distribution Determination

[0036] The whole interpolymer product samples and the individual interpolymer samples are analyzed by gel permeation chromatography (GPC) on a Waters 150C high temperature chromatographic unit equipped with three mixed porosity columns (Polymer Laboratories 10<sup>3</sup>, 10<sup>4</sup>, 10<sup>5</sup>, and 10<sup>6</sup>), operating at a system temperature of 140°C. The solvent is 1,2,4-trichlorobenzene, from which 0.3 percent by weight solutions of the samples are prepared for injection. The flow rate is 1.0 milliliters/minute and the injection size is 200 microliters.

[0037] The molecular weight determination is deduced by using narrow molecular weight distribution polystyrene standards (from Polymer Laboratories) in conjunction with their elution volumes. The equivalent polyethylene molecular weights are determined by using appropriate Mark-Houwink coefficients for polyethylene and polystyrene (as described by Williams and Ward in Journal of Polymer Science, Polymer Letters, Vol. 6, (621) 1968) to derive the following equation:

$$M_{\text{polyethylene}} = a \cdot (M_{\text{polystyrene}})^b$$

In this equation,  $a = 0.4316$  and  $b = 1.0$ . Weight average molecular weight,  $M_w$ , is calculated in the usual manner according to the following formula:  $M_w = \sum w_i \cdot M_i$ , where  $w_i$  and  $M_i$  are the weight fraction and molecular weight, respectively, of the  $i^{\text{th}}$  fraction eluting from the GPC column.

[0038] The molecular weight distribution ( $M_w/M_n$ ) for the homogeneously branched linear or homogeneously branched substantially linear olefin polymers of the invention is from 1.5 to 2.5, and especially from 1.7 to 2.3.

#### Processing Index Determination

[0039] The rheological processing index (PI) is measured by a gas extrusion rheometer (GER). The GER is described by M. Shida, R.N. Shroff and L.V. Cancio in *Polym. Eng. Sci.*, Vol. 17, no. 11, p. 770 (1977), and in "Rheometers for Molten Plastics" by John Dealy, published by Van Nostrand Reinhold Co. (1982) on page 97-99. The processing index is measured at a temperature of 190°C, at nitrogen pressure of 2500 psig (17.2 MPa) using a 0.0296 inch (752 micrometers) diameter, 20:1 L/D die having an entrance angle of 180°. The GER processing index is calculated in millipoise units from the following equation:

$$PI = 2.15 \times 10^6 \text{ dynes/cm}^2 / (1000 \times \text{shear rate}),$$

where:  $2.15 \times 10^6 \text{ dynes/cm}^2$  ( $2.15 \times 10^5 \text{ Pa}$ ) is the shear stress at 2500 psi (17.2 MPa), and the shear rate is the shear rate at the wall as represented by the following equation:

$$32 Q' / (60 \text{ sec/min}) (0.745) (\text{Diameter} \times 2.54 \text{ cm/in})^3,$$

where:

$Q'$  is the extrusion rate (gms/min),  
 0.745 is the melt density of polyethylene (gm/cm<sup>3</sup>), and  
 Diameter is the orifice diameter of the capillary (inches).

The PI is the apparent viscosity of a material measured at apparent shear stress of  $2.15 \times 10^6$  dyne/cm<sup>2</sup> ( $2.15 \times 10^5$  Pa.).

[0040] For the substantially linear ethylene polymers used herein, the PI is less than or equal to 70 percent of that of a comparative linear ethylene polymer at about the same  $I_2$  and  $M_w/M_n$ .

[0041] An apparent shear stress vs. apparent shear rate plot is used to identify the melt fracture phenomena. According to Ramamurthy in *Journal of Rheology*, 30(2), 337-357, 1986, above a certain critical flow rate, the observed extrudate irregularities may be broadly classified into two main types: surface melt fracture and gross melt fracture.

[0042] Surface melt fracture occurs under apparently steady flow conditions and ranges in detail from loss of specular gloss to the more severe form of "sharkskin". In this disclosure, the onset of surface melt fracture is characterized at the beginning of losing extrudate gloss at which the surface roughness of extrudate can only be detected by 40X magnification. The critical shear rate at onset of surface melt fracture for the substantially linear ethylene polymers is at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear ethylene polymer having about the same  $I_2$ ,  $M_w/M_n$ , and density. For the purposes of the instant application, "about the same" means that the  $I_2$ ,  $M_w/M_n$ , and density values of both the substantially linear ethylene polymer and the linear ethylene polymer to which it is compared is within 10 percent of each other. Preferably, the critical shear stress at onset of surface melt fracture for the substantially linear olefin polymers of the invention is greater than  $2.8 \times 10^6$  dynes/cm<sup>2</sup> ( $2.8 \times 10^5$  Pa.)

[0043] Gross melt fracture occurs at unsteady flow conditions and ranges in detail from regular (alternating rough and smooth, helical, etc.) to random distortions. For commercial acceptability, (for example, in blown film products), surface defects should be minimal, if not absent. The critical shear rate at onset of surface melt fracture (OSMF) and critical shear stress at onset of gross melt fracture (OGMF) will be used herein based on the changes of surface roughness and configurations of the extrudates extruded by a GER. For the substantially linear olefin polymers used in the invention, the critical shear stress at onset of gross melt fracture is preferably greater than  $4 \times 10^6$  dynes/cm<sup>2</sup> ( $4 \times 10^5$  Pa.)

[0044] The homogeneously branched linear or homogeneously branched substantially linear polymers useful in the present invention can be homopolymers of  $C_2$ - $C_{20}$   $\alpha$ -olefins, such as ethylene, propylene, 4-methyl-1-pentene, etc., or they can be interpolymers of ethylene with at least one  $C_3$ - $C_{20}$   $\alpha$ -olefin and/or  $C_2$ - $C_{20}$  acetylenically unsaturated monomer and/or  $C_4$ - $C_{18}$  diolefins. The substantially linear polymers of the present invention can also be interpolymers of ethylene with at least one of the above  $C_3$ - $C_{20}$   $\alpha$ -olefins, diolefins and/or acetylenically unsaturated monomers in combination with other unsaturated monomers. The term "interpolymer" means that the polymer has at least two comonomers (for example, a copolymer) and also includes more than two comonomers (for example, terpolymers). Substantially linear ethylene/ $\alpha$ -olefin copolymers are preferred however, and ethylene/ $C_3$ - $C_{20}$   $\alpha$ -olefin copolymers are especially preferred.

#### Suitable Blowing Agents

[0045] Foaming agents suitable for use in the gaskets disclosed herein include physical blowing agents which function as gas sources by going through a change of physical state. Volatile liquids produce gas by passing from the liquid to gaseous state, whereas compressed gases are dissolved under pressure in the melted polymer. Chemical blowing agents produce gas by a chemical reaction, either by a thermal decomposition or by a reaction between two components.

[0046] Suitable physical blowing agents include pentanes (for example, n-pentane, 2-methylbutane, 2,2-dimethylpropane, 1-pentane and cyclopentane), hexanes (for example, n-hexane, 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane, 2,2-dimethylbutane, 1-hexene, cyclohexane), heptanes (for example, n-heptane, 2-methylhexane, 2,2-dimethylpentane, 2,3-dimethylpentane, 2,4-dimethylpentane, 3,3-dimethylpentane, 3-ethylpentane, 2,2,3-trimethylbutane, 1-heptene), benzene, toluene, dichloromethane, trichloromethane, trichloroethylene, tetrachloromethane, 1,2-dichloroethane, trichlorofluoromethane, 1,1,2-trichlorotrifluoroethane, methanol, ethanol, 2-propanol, ethyl ether, isopropyl ether, acetone, methyl ethyl ketone, and methylene chloride.

[0047] Suitable gaseous blowing agents include carbon dioxide and nitrogen.

[0048] Suitable chemical blowing agents include sodium bicarbonate, dinitrosopentamethylenetetramine, sulfonylhydrazides, azodicarbonamide (for example, Celogen™ A7 130 made by Uniroyal Chemical), p-toluenesulfonyl sem-

icarbazide, 5-phenyltetrazole, diisopropylhydrazodicarboxylate, 5-phenyl-3,6-dihydro-1,3,4-oxadiazin-2-one, and sodium borohydride.

**[0049]** The amount of blowing agent is dependent on the desired density reduction. One can calculate the amount of blowing agent required by knowing the volume of gas produced per gram of blowing agent at a given temperature and the desired density reduction (or target density) for a desired application. For chemical blowing agents the range is 0.1 to 4 percent by weight and more preferably 0.25 to 2 percent by weight. This range can also be adjusted by the addition of activation agents (sometimes referred to as coagents) such as (zinc oxide, zinc stearate). Preferably, the coagent is used in the formulation such that, for example, the zinc oxide is used at a level of one and one-half to twice that of the blowing agent (for example, azodicarbonamide).

**[0050]** Foams useful for making the gaskets claimed herein can be made as described in the following U.S. Patents: 5,288,762; USP 5,340,840; USP 5,369,136; USP 5,387,620 and USP 5,407,965.

#### Suitable Gasket Configurations

**[0051]** Gaskets can have many different forms, including "o-rings" and flat seals (for example, "film-like" gaskets having a thickness commensurate with the intended use).

**[0052]** Suitable end uses include gaskets for metal and plastic closures, as well as other gasket applications. These applications include beverage cap liners, hot fill juice cap liners, polypropylene cap liners, steel or aluminum cap liners, high density polyethylene cap liners, window glass gaskets, sealed containers, closure caps, gaskets for medical devices, filter elements, pressure venting gaskets, hot melt gaskets, easy twist off caps, electrochemical cell gaskets, refrigerator gaskets, galvanic cell gaskets, leak proof cell gaskets, waterproofing sheet, reusable gaskets, synthetic cork like materials, thin cell electromembrane separator, magnetic rubber materials, disc gaskets for alcoholic beverage bottle caps, freeze resistant seal rings, gaskets for plastic castings, expansion joints and waterstops, corrosion-resistant conduit connectors, flexible magnetic plastics, pipe joint seals, integral weatherproof plastic lid and hinge for electrical outlets, magnetic faced foamed articles, jar rings, flexible gaskets, glass seals, tamper evident sealing liners, pressure applicators, combined bottle cap and straw structures, large condiment bottle liners, metal caps for applesauce or salsa jars, home canning jars, and "crowns."

**[0053]** Gaskets made from the homogeneously branched linear or homogeneously branched substantially linear ethylene polymers have numerous advantages, especially when used in food-stuff applications. These include: improved taste and odor over incumbent polymer gaskets such as ethylene/vinyl acetate; low adhesion to polar substrates (for example, polyethylene terephthalate, glass) which is useful for low torque removal of the closure/cap; low extractables (for example, less than about 5.5 percent by weight) (also useful for food-stuffs, especially regarding regulatory compliance); good adhesion to non-polar substrates (for example, polypropylene and high density polyethylene (either linear homopolymer polyethylene or linear heterogeneous high density polyethylene)).

**[0054]** Good adhesion in a cap or crown can be described as sufficiently adhering to the substrate. A liner exhibits this type adhesion when it can only be removed under a cohesive failure mode. Adhesion to metal (such as beer crowns) requires a lacquer that is both compatible with the polymer system and bonds to the metal (for example, a lacquer such as AL 1296-01M sold by W.R. Grace). One such example that provides good adhesion is a modified polyester provided by Watson Standard (#40-207 or #40-542). Modified epoxy lacquers have also demonstrated good adhesion.

**[0055]** Additional benefits include adequate gas and water barrier properties; high melting point relative to incumbent polymers (for example, ethylene/vinyl acetate); good stress crack resistance; good chemical resistance; variable hardness (useful for specific packaging which may require more or less gasket stiffness, depending on the degree of torque required to seal the container and the internal pressure of the container); and most importantly, for the homogeneously branched substantially linear ethylene polymers, excellent processability achieved by uniquely controlling the melt flow ratio ( $I_{10}/I_2$ ) independently of the molecular weight distribution ( $M_w/M_n$ ). Substantially linear ethylene polymers having  $M_w/M_n$  from 1.5 to 2.5, and  $I_{10}/I_2$  ratios from 7 to as high as 20 are particularly useful in these gasketing applications.

**[0056]** Various gasket manufacturing techniques include those disclosed in USP 5,215,587 (McConnellogue et al.); USP 4,085,186 (Rainer); USP 4,619,848 (Knight et al.); USP 5,104,710 (Knight); USP 4,981,231 (Knight); USP 4,717,034 (Mumford); USP 3,786,954 (Shull); USP 3,779,965 (Lefforge et al.); USP 3,493,453 (Ceresa et al.); USP 3,183,144 (Caviglia); USP 3,300,072 (Caviglia); USP 4,984,703 (Burzynski); USP 3,414,938 (Caviglia); USP 4,939,859 (Bayer); USP 5,137,164 (Bayer); and USP 5,000,992 (Kelch). Preferably, the gasket is made in a single step process by extruding a portion of the foaming substantially linear ethylene polymer and then immediately compression molding that portion into a gasket.

**[0057]** The one-step process used for forming and foaming gaskets disclosed herein is different from processes used for making gaskets by extruded sheets or films by conventional techniques as blown, cast or extrusion coated films, followed by stamping or cutting the gasket from the sheet or film since substantial waste is avoided and more control over gasket dimensions in 1-step process: another advantage of the 1-step process is achieving lower gasket



thickness (for example, from 5 mils to 50 mils (from 0.13 to 1.3 mm)).

[0058] Preferably, the one step process for forming a gasket having a Shore A hardness from 40 to 95, comprising the steps of:

- 5 (a) combining at least one homogeneously branched linear or a homogeneously branched substantially linear ethylene polymer with at least one blowing agent to form a mixture,
- (b) extruding said mixture through an orifice,
- (c) cutting the extruded mixture into a pellet,
- (d) positioning the cut extruded mixture into a closure, and
- 10 (e) compression shaping the positioned mixture in said closure.

[0059] More preferably, for closures having a 28mm diameter, the cut pellet weighs from 120mg to 300mg.

[0060] Multilayer film structures are also suitable for making the gaskets disclosed herein, with the proviso that at least one layer (preferably the inner layer which is located adjacent to the product) comprises the homogeneously branched linear or homogeneously branched substantially linear ethylene polymer. Foamed multilayer gaskets comprising the homogeneously branched linear or homogeneously branched substantially linear ethylene polymers are also useful in the present invention.

#### Examples 1-6 and Comparative Examples 1\*-10\*

[0061] Polymers 1 and 2 and comparison polymers 3-6 are tested for compression set at ambient temperature (about 25°C) and at elevated temperature (60°C). Polymers 1 and 2 are ethylene/1-octene substantially linear polyethylenes produced by the constrained geometry catalyst technology, as described in USP 5,272,236 and are tested with varying amounts of a blowing agent (Celogen™ AZNP made by Uniroyal Chemical). Polymer 1 has a melt index ( $I_2$ ) of 30 g/10 minutes, a density of about 0.903 g/cm<sup>3</sup>, a melt flow ratio,  $I_{10}/I_2$ , of 7.1 and a molecular weight distribution,  $M_w/M_n$ , of 2.04. Polymer 2 has a melt index ( $I_2$ ) of 30 g/10 minutes, a density of 0.913 g/cm<sup>3</sup>, a melt flow ratio,  $I_{10}/I_2$ , of 7.1 and a molecular weight distribution,  $M_w/M_n$ , of 2.14.

[0062] The powdered blowing agent is incorporated into each of polymers 1 and 2 by preparing 20 pound (9 kg) lots of dry blends of the blowing agent with each polymer. The dry blends are prepared by preweighing and then adding the ingredients into a large bag and vigorously shaking the sample until a homogeneous blend is observed, usually after shaking 3 minutes. In order to account for some small loss of the blowing agent on the sidewall of the bag, the blowing agent is added at levels of 110 percent of that targeted for a particular blend.

[0063] The foamed samples are prepared on a DEMAG injection molding machine at a melt temperature of 410°F (210°C). Instead of injecting the shot into a mold, the shot is injected onto a piece of polyester film (for example, Mylar™ made by E.I. Du Pont de Nemours & Company). The foam is then allowed to freely expand and cool to room temperature (about 25°C).

[0064] Comparison polymer 3 is a heterogeneous linear low density polyethylene (LLDPE) having a melt index of 25.6 g/10 minutes, a density of 0.918 g/cm<sup>3</sup>, a melt flow ratio,  $I_{10}/I_2$ , of 7 and a molecular weight distribution,  $M_w/M_n$ , of 2.9. Comparison polymer 4 is an ethylene/vinyl acetate copolymer made by E.I. Du Pont de Nemours & Company, and has 11 percent vinyl acetate content. Comparison polymer 5 is an ethylene vinyl acetate copolymer trademarked Elvax™ 650, made by E.I. Du Pont de Nemours & Company, and has 12 percent vinyl acetate content and a melt index of 8 g/10 minutes and a density of 0.933 g/cc. Comparison polymer 6 is a melt blend of plasticized polyvinylchloride (PVC) and a blowing agent as provided by a compounder. This material has 35 percent plasticizer (di(2-ethylhexyl) phthalate), a density of 1.19 g/cc and a shore A hardness of 65. Comparison polymer 7 is a melt blend of PVC and blowing agent prepared by physically combining and extruding the materials.

[0065] Compression set is tested in accordance with ASTM D-395, method B, type 1 test specimens. Shore A is tested as described supra. Table 3 summarizes compression set and Shore A hardness data for polymers 1 and 2 and comparative polymers 3-7 with varying amounts of blowing agent incorporated:

Table 3

Example (polymer used)	Percent blowing agent added to polymer	Compression Set at 25°C (percent lost)	Compression Set at 60°C (percent lost)	Shore A	Density (g/cc)	Density Reduction (percent)
1* (1)	0	30.0	71.5	94	0.903	0
1 (1)	0.25	18.2	66.1	89	0.493	45.4
2 (1)	0.5	17.6	65.6	60	0.411	54.5
3(1)	1	14.8	65.1	45	0.317	64.9
2* (2)	0	30.3	69.5	96	0.913	0
4 (2)	0.25	28.8	65.6	92	0.561	38.6
5 (2)	0.5	24.0	59.2	75	0.358	60.8
6(2)	1	21.4	64.4	75	0.321	64.8
3* (3)	0	32.9	72.3	95	0.918	0
4* (3)	0.25	32.3	70.9	92	0.581	43.6
5* (3)	0.5	32.3	68.3	NM	0.359	60.9
6* (3)	1	31.9	67.9	NM	0.339	63.1
7* (4)	0	26.5	76.3	94	0.943	0
8* (5)	0	38.4	75.2	N/A	NM	0
9* (6)	1	30.3	65.8	70	1.191	0
10* (7)	1	2.9	60	NM	0.608	49.5

\*Comparison Example Only; not an example of the invention

N/A = Not Applicable

NM = Not Measured

[0066] The results indicate that there is a significant improvement in compression set and hardness of the homogeneous linear polyethylenes due to foaming. There is a significant decrease in the percentage loss for compression set and in the Shore A hardness. The resulting compression set and hardness properties are in some cases significantly better for the foamed homogeneous linear polyethylenes than for incumbent materials used in closure liner applications. Examples 1-3 and 4-6 exhibit lower ambient temperature compression set than comparative examples 1\*- 6\*, and 8\*. Examples 1-3 and 4-6 exhibit lower compression set at 60°C than comparative examples 1\* - 8\*. Examples 1-3 and 4-6 exhibit lower Shore A hardness than comparative examples 1\*- 4\*, and 7\*. Although not all of the comparison examples are foamed, the comparison is still valid because the requirements for applications are typically minimums or threshold value above or below which the materials need to be. Further, the most important comparison is between the foamed homogeneously branched substantially linear ethylene substantially linear ethylene polymers and unfoamed heterogeneously branched linear ethylene polymers and the foamed heterogeneously branched linear ethylene polymers samples.

#### Claims

1. A foamed gasket characterized as comprising at least one homogeneously branched ethylene polymer and at least one blowing agent, wherein the polymer has a density of from 0.85 to 0.93 g/cm<sup>3</sup>, and is characterized as having a molecular weight distribution  $M_w/M_n$  of from 1.5 to 2.5 and as having a CDBI (Composition Distribution Branch Index) greater than 50 percent, which CDBI is calculated from data obtained by temperature rising elution fractionation.
2. The gasket of claim 1, wherein the ethylene polymer is a substantially linear ethylene polymer having a polymer backbone which is substituted with from 0.01 to 3 long chain branches per 1000 carbons, which is further characterized as having:

- a) a melt flow ratio,  $I_{10}/I_2 \geq 5.63$ , with  $I_{10}$  being determined in accordance with ASTM D-1238, Condition 190°C/10 kg and  $I_2$  being determined in accordance with ASTM D-1238, Condition 190°C/2.16 kg,  
b) a molecular weight distribution,  $M_w/M_n$ , defined by the equation:

$$M_w/M_n \leq (I_{10}/I_2) - 4.63,$$

and

- c) a critical shear stress at onset of gross melt fracture greater than  $4 \times 10^6$  dynes/cm<sup>2</sup> ( $4 \times 10^5$  Pa.), as determined using a gas extrusion rheometer.

3. The gasket of Claim 1, wherein the ethylene polymer is a homogeneously branched linear ethylene polymer, which is further characterized as having less than 0.01 long chain branch per 1000 carbons.

4. The foamed gasket of any of the preceding claims, wherein the homogeneously branched ethylene polymer is:

- (A) an ethylene homopolymer, or  
(B) an interpolymers of ethylene with at least one C<sub>3</sub>-C<sub>20</sub> alpha-olefin.

5. The foamed gasket of claim 4 wherein the homogeneously branched ethylene polymer is a copolymer of ethylene with a C<sub>3</sub>-C<sub>20</sub> alpha-olefin.

6. The foamed gasket of any of the preceding claims, wherein the homogeneously branched ethylene polymer has a density from 0.895 g/cm<sup>3</sup> to 0.915 g/cm<sup>3</sup>.

7. The foamed gasket of any of the preceding claims, wherein the foaming agent is a physical blowing agent, gaseous blowing agent or chemical blowing agent.

8. The foamed gasket of any of the preceding claims, wherein the foaming agent is sodium bicarbonate, dinitrosopentamethylenetetramine, sulfonyl hydrazides, azodicarbonamide, p-toluenesulfonyl semicarbazide, 5-phenyltetrazole, diisopropylhydrazodicarboxylate, 5-phenyl-3,6-dihydro-1,3,4-oxadiazin-2-one, or sodium borohydride.

9. The foamed gasket of any of the preceding claims, wherein the foaming agent is carbon dioxide or nitrogen.

10. The foamed gasket of any of the preceding claims, wherein the foaming agent is a pentane, hexane, heptane, benzene, toluene, dichloromethane, trichloromethane, trichloroethylene, tetrachloromethane, 1,2-dichloroethane, trichlorofluoromethane, 1,1,2-trichlorotrifluoroethane, methanol, ethanol, 2-propanol, ethyl ether, isopropyl ether, acetone, methyl ethyl ketone; methylene chloride; isobutane; n-butane; or 1, 1-difluoroethane.

11. A one-step process of forming a gasket having a Shore A hardness, as measured using ASTM D-2240, of from 40 to 95, which is characterized by the steps of:

- (A) combining at least one homogeneously branched ethylene polymer having a density of from 0.85 to 0.93 g/cm<sup>3</sup>, which is characterized as having a molecular weight distribution  $M_w/M_n$  of from 1.5 to 25 and as having a CDBI greater than 50 percent with at least one blowing agent to form a mixture,

(B) extruding said mixture through an orifice,

(C) cutting the extruded mixture into a pellet,

(D) positioning the cut extruded mixture into a closure, and

(E) compression shaping the positioned mixture in said closure.

12. The process of claim 11 wherein the cut pellet weighs from 120 mg to 300 mg.

#### Patentansprüche

1. Geschäumte Dichtung, **dadurch gekennzeichnet**, dass sie wenigstens ein homogen verzweigtes Ethylenpolymer und wenigstens ein Treibmittel umfasst, wobei das Polymer eine Dichte von 0.85 bis 0.93 g/cm<sup>3</sup> besitzt und da-

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durch gekennzeichnet ist, dass es eine Molekulargewichtsverteilung  $M_w/M_n$  von 1,5 bis 2,5 besitzt und dass es einen CDBI (Zusammensetzungsverteilungsverzweigungsindex) von größer als 50 % besitzt, wobei der CDBI von Daten berechnet wird, die durch Temperaturanstiegselutionsfraktionierung erhalten wurden.

- 5 2. Dichtung nach Anspruch 1, wobei das Ethylenpolymer ein im Wesentlichen lineares Ethylenpolymer ist, das ein Polymergrundgerüst besitzt, das mit 0,01 bis 3 Langkettenverzweigungen pro 1000 Kohlenstoffatome substituiert ist, das weiter **dadurch gekennzeichnet** ist, dass es:

- 10 a) ein Schmelzflussverhältnis,  $I_{10}/I_2 \geq 5,63$ , wobei  $I_{10}$  gemäß ASTM D-1238, Bedingung 190 °C/10 kg bestimmt wird und  $I_2$  gemäß ASTM D-1238, Bedingung 190 °C/2,16 kg bestimmt wird,  
b) eine Molekulargewichtsverteilung,  $M_w/M_n$ , definiert durch die Gleichung:

$$M_w/M_n \leq (I_{10}/I_2) - 4,63$$

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und

- c) eine kritische Scherbeanspruchung bei Einsetzen von Gesamtschmelzbruch von größer als  $4 \times 10^6$  dyne/cm<sup>2</sup> ( $4 \times 10^5$  Pa), wie unter Verwendung eines Gasextrusionsrheometers bestimmt,

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aufweist.

3. Dichtung nach Anspruch 1, wobei das Ethylenpolymer ein homogen verzweigtes, lineares Ethylenpolymer ist, das weiter **dadurch gekennzeichnet** ist, dass es weniger als 0,01 Langkettenverzweigungen pro 1000 Kohlenstoffatome aufweist.

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4. Geschäumte Dichtung nach einem der vorhergehenden Ansprüche, wobei das homogen verzweigte Ethylenpolymer

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(A) ein Ethylenhomopolymer oder

(B) ein Interpolymer aus Ethylen mit wenigstens einem C<sub>3</sub>-C<sub>20</sub>-Alpha-Olefin ist.

5. Geschäumte Dichtung nach Anspruch 4, wobei das homogen verzweigte Ethylenpolymer ein Copolymer aus Ethylen mit einem C<sub>3</sub>-C<sub>20</sub>-Alpha-Olefin ist.

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6. Geschäumte Dichtung nach einem der vorhergehenden Ansprüche, wobei das homogen verzweigte Ethylenpolymer eine Dichte von 0,895 g/cm<sup>3</sup> bis 0,915 g/cm<sup>3</sup> aufweist.

7. Geschäumte Dichtung nach einem der vorhergehenden Ansprüche, wobei das Schäummittel ein physikalisches Treibmittel, ein gasförmiges Treibmittel oder ein chemisches Treibmittel ist.

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8. Geschäumte Dichtung nach einem der vorhergehenden Ansprüche, wobei das Schäummittel Natriumbicarbonat, Dinitrosopentamethylentetramin, Sulfonylhydrazide, Azodicarbonamid, p-Toluolsulfonylsemicarbazid, 5-Phenyltetrazol, Diisopropylhydrazodicarboxylat, 5-Phenyl-3,6-dihydro-1,3,4-oxadiazin-2-on oder Natriumborhydrid ist.

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9. Geschäumte Dichtung nach einem der vorhergehenden Ansprüche, wobei das Schäummittel Kohlendioxid oder Stickstoff ist.

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10. Geschäumte Dichtung nach einem der vorhergehenden Ansprüche, wobei das Schäummittel Pentan, Hexan, Heptan, Benzol, Toluol, Dichlormethan, Trichlormethan, Trichlorethylen, Tetrachlormethan, 1,2-Dichlorethan, Trichlorfluormethan, 1,1,2-Trichlortrifluorethan, Methanol, Ethanol, 2-Propanol, Ethylether, Isopropylether, Aceton, Methylalketon, Methylenchlorid, Isobutan, n-Butan oder 1,1-Difluorethan ist.

11. Einschrittverfahren zur Bildung einer Dichtung, die eine Shore A-Härte, wie gemessen unter Verwendung von ASTM D-2240, von 40 bis 95 aufweist, welches durch die folgenden Schritte gekennzeichnet ist:

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- (A) Kombinieren von wenigstens einem homogen verzweigten Ethylenpolymer, das eine Dichte von 0,85 bis 0,93 g/cm<sup>3</sup> besitzt, dass **dadurch gekennzeichnet** ist, dass es eine Molekulargewichtsverteilung  $M_w/M_n$  von 1,5 bis 2,5 besitzt und dass es einen CDBI größer als 50 % besitzt mit wenigstens einem Treibmittel, um eine

- Mischung zu bilden,  
 (B) Extrudieren der Mischung durch kleine Öffnung,  
 (C) Schneiden der extrudierten Mischung in ein Granulat,  
 (D) Anordnen der geschnittenen, extrudierten Mischung in einen Verschluss und  
 (E) Kompressionsformen der angeordneten Mischung in diesem Verschluss.

12. Verfahren nach Anspruch 11, wobei das geschnittene Granulat von 120 mg bis 300 mg wiegt.

## 10 Revendications

1. Joint d'étanchéité en mousse **caractérisé en ce qu'il** comprend au moins un polymère d'éthylène ramifié de manière homogène et au moins un agent gonflant, dans lequel le polymère a une densité comprise entre 0,85 et 0,93 g/cm<sup>3</sup>, et est caractérisé comme ayant une répartition de masse moléculaire  $M_w/M_n$  comprise entre 1,5 et 2,5 et  
 15 comme ayant un IRDS (Indice de ramification de distribution structurale) supérieur à 50 pour-cent, lequel IRDS est calculé à partir des données obtenues par fractionnement par élution avec élévation de température.

2. Joint d'étanchéité selon la revendication 1, dans lequel le polymère d'éthylène est un polymère d'éthylène sensiblement linéaire ayant un squelette de polymère qui est substitué par de 0,01 à 3 ramifications à chaîne longue pour 1000 carbones, qui est en plus caractérisé comme ayant :

- a) un rapport de fluidité à l'état fondu,  $I_{10}/I_2 \geq 5,63$ ,  $I_{10}$  étant déterminé conformément à l'ASTM D-1238, Condition 190°C/10 kg et  $I_2$  étant déterminé conformément à l'ASTM D-1238, Condition 190°C/2,16 kg,  
 b) une répartition de masse moléculaire,  $M_w/M_n$ , définie par l'équation :

$$M_w/M_n \leq (I_{10}/I_2) - 4,63,$$

et

c) une contrainte de cisaillement critique au commencement des fractures de coulées dans la masse supérieure à  $4 \times 10^6$  dynes/cm<sup>2</sup> ( $4 \times 10^5$  Pa.), comme déterminée en utilisant un rhéomètre d'extrusion à gaz.

3. Joint d'étanchéité selon la revendication 1, dans lequel le polymère d'éthylène est un polymère d'éthylène linéaire ramifié de manière homogène, qui est en plus caractérisé comme ayant moins de 0,01 ramification à chaîne longue pour 1000 carbones.

4. Joint d'étanchéité en mousse selon l'une quelconque des revendications précédentes, dans lequel le polymère d'éthylène ramifié de manière homogène est :

- (A) un homopolymère d'éthylène, ou  
 (B) un interpolymère d'éthylène avec au moins une alpha-oléfine en C<sub>3</sub>-C<sub>20</sub>.

5. Joint d'étanchéité en mousse selon la revendication 4, dans lequel le polymère d'éthylène ramifié de manière homogène est un copolymère d'éthylène avec une alpha-oléfine en C<sub>3</sub>-C<sub>20</sub>.

6. Joint d'étanchéité en mousse selon l'une quelconque des revendications précédentes, dans lequel le polymère d'éthylène ramifié de manière homogène présente une densité comprise entre 0,895 g/cm<sup>3</sup> et 0,915 g/cm<sup>3</sup>.

7. Joint d'étanchéité en mousse selon l'une quelconque des revendications précédentes, dans lequel l'agent gonflant est un agent gonflant physique, un agent gonflant gazeux ou un agent gonflant chimique.

8. Joint d'étanchéité en mousse selon l'une quelconque des revendications précédentes, dans lequel l'agent gonflant est le bicarbonate de sodium, le dinitrosopentaméthylènetétramine, les hydrazides de sulfonyle, l'azodicarbonamide, le semi-carbazide de p-toluènesulfonyle, le 5-phényltétrazole, le diisopropylhydrazodicarboxylate, le 5-phényl-3,6-dihydro-1,3,4-oxadiazin-2-one et le borohydrure de sodium.

9. Joint d'étanchéité en mousse selon l'une quelconque des revendications précédentes, dans lequel l'agent gonflant est le dioxyde de carbone ou l'azote.

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10. Joint d'étanchéité en mousse selon l'une quelconque des revendications précédentes, dans lequel l'agent gonflant est un pentane, un hexane, un heptane, le benzène, le toluène, le dichlorométhane, le trichlorométhane, le trichloroéthylène, le tétrachlorométhane, le 1,2-dichloroéthane, le trichlorofluorométhane, le 1,1,2-trichlorotrifluoroéthane, le méthanol, l'éthanol, le 2-propanol, l'éther éthylique, l'éther isopropylique, l'acétone, le méthyléthyl-kétone ; le chlorure de méthylène ; l'isobutane ; le n-butane ; ou le 1,1-difluoroéthane.
11. Procédé en une seule étape pour former un joint d'étanchéité ayant une dureté Shore A, telle que mesurée en utilisant l'ASTM D-2240, de 40 à 95, procédé caractérisé par les étapes consistant à :
- (A) combiner au moins un polymère d'éthylène ramifié de manière homogène, ayant une densité comprise entre 0,85 et 0,93 cm<sup>3</sup>, caractérisé comme ayant une répartition de masse moléculaire  $M_w/M_n$  comprise entre 1,5 et 2,5 et comme ayant un IRDS supérieur à 50 pour-cent, avec au moins un agent gonflant pour former un mélange,
  - (B) extruder ledit mélange à travers un orifice,
  - (C) découper le mélange extrudé en une pastille,
  - (D) placer le mélange extrudé découpé dans une fermeture, et
  - (E) façonner par compression le mélange placé dans ladite fermeture.
12. Procédé selon la revendication 11, dans lequel la pastille découpée pèse entre 120 mg et 300 mg.